Electronic Supporting Information

Proton reduction by molecular catalysts in water under demanding atmospheres

David W. Wakerley, Manuela A. Gross and Erwin Reisner*

Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

E-mail: reisner@ch.cam.ac.uk

Contents
Experimental Section page S2
Supporting Figures page S3
Supporting Tables page S6
Supporting References page S7
Experimental Section

**Reagents.** All chemical reagents were obtained from commercial suppliers at the highest available purity for analytical measurements. All solvents were HPLC grade and Millipore water was used in all electrochemical analysis. \( [\text{Ni} \left( \text{P}^2\text{N}^\text{Ph}_2 \text{P}^\text{OH} \text{PhCH}_2 \text{P}^\text{O} \right) \text{Br}_2 \cdot \text{HBr}] \text{NiP} \) and \( (\text{Et}_3 \text{NH}) \left[ \text{Co}^\text{III} \text{Cl}(\text{dimethylglyoximato})_2(\text{pyridyl-4-hydrophosphonate}) \right] \text{CoP} \) were synthesised as described previously. Buffer solutions were acidified to the desired pH using dilute H2SO4.

**General Electrochemistry.** Electrochemistry was carried out with a potentiostat (iVium/ PalmSens) in a three-electrode cell configuration. All solutions were purged for at least 10 min and measurements were taken at room temperature in buffered electrolyte solutions of triethanolamine (TEOA) and Na2SO4 (0.1 M each, pH 7) or trisodium citrate (0.1 M, pH 4.5). Potentials were converted to NHE according to the relationship \( E \text{ (vs. NHE)} = E \text{ (vs. Ag/AgCl(KCl sat)}} + 0.197 \text{ V.} \)

**Cyclic Voltammetry.** Cyclic voltammograms (CVs) were recorded at 100 mV s⁻¹ using a 3 mm diameter glassy carbon disk working, a Pt-mesh counter and Ag/AgCl(KCl sat) reference electrode (BASi) in a single compartment cell. Each voltammogram was started at 0.7 V vs. NHE and the second consecutive scan is presented in all figures.

**Controlled Potential Electrolysis (CPE).** CPE was performed in a 3-electrode cell configuration during vigorous stirring. CPE of \text{NiP} and \text{CoP} was performed with a glassy carbon rod (1.96 cm²) working electrode, a Pt-mesh counter contained in a fritted-glass compartment and a Ag/AgCl reference electrode using 2.5 mL of solution in an air-tight cell (5.4 mL headspace) containing 0.5 mM of catalyst. CPE with a Pt working electrode (1 mm diameter) was undertaken using a single compartment cell with no catalyst in solution and a Pt-mesh counter and a Ag/AgCl reference electrode. \( \text{H}_2 \) was quantified by gas chromatography and each experiment was carried out at least three times. The standard deviation (\( \sigma \)) was calculated according to Eq. 1 and the Faradaic efficiency according to Eq. 2:

\[
\sigma = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}} \quad \text{(Eq. 1)}
\]

\[
\text{FE (\%)} = \frac{\text{H}_2 \text{ (mol)} \times 2 \times F \text{ (C mol}^{-1})}{\text{Charge Passed Through WE (C)}} \times 100 \quad \text{(Eq. 2)}
\]

**Gas Chromatographic Analysis.** Gas chromatography was carried out on an Agilent 7890A gas chromatograph with a 5 Å molecular sieve column at 45 °C and \( \text{N}_2 \) carrier gas with a flow rate of approximately 3 mL min⁻¹. Methane (2% CH₄ in \( \text{N}_2 \)) was used as an external standard.

**Spectroelectrochemistry.** IR and UV/visible-spectroelectrochemistry was carried out using a cell designed by the authors of Ref 4. The cell contained Pt mesh working and counter electrodes with a Ag/Ag⁺ reference electrode. Spectra were taken using solutions of \([\text{CoCl(dmgH)}_2(4\text{-methoxypyridine})]\) (5 mM for IR; 0.25 mM for UV-visible spectra) or \text{NiP} (1.25 mM for IR; 0.25 mM for UV-visible spectra) with tetrabutyl ammonium bromide (0.3
M) in MeOH, which was saturated with CO. IR spectra were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer and UV-visible spectra were recorded on a Varian Cary 50 UV-visible spectrometer. In each experiment the working electrode was held at a defined potential until the current stabilised (typically 60 s) and an IR spectrum was recorded. This was repeated in 50 mV intervals over a range of potentials. 

**Supporting Figures**

**Figure S1.** H₂ inhibition study (100% H₂ vs. 100% N₂ atmosphere) on a glassy carbon working electrode at 100 mV s⁻¹ with (a) NiP (1 mM) in citrate buffer (0.1 M, pH 4.5) and (b) CoP (1 mM) in TEOA/Na₂SO₄ (0.1 M each, pH 7).

**Figure S2.** The effect of O₂ on the Co™/Co™ redox wave of CoP (1 mM) in TEOA/Na₂SO₄ (0.1 M each, pH 7) at 100 mV s⁻¹ on a glassy carbon working electrode.
Figure S3. \(I-t\) trace from a Pt working electrode in 0.1 M citrate buffer at pH 4.5 held at -0.4 V \textit{vs.} NHE in 100% CO and a subsequent electrolysis under 100% N\(_2\).

Figure S4. \(I-t\) traces and \(\text{H}_2\) produced by CoP (1 mM) in 100% CO (top) and subsequently after purging with 100% N\(_2\) (bottom). Experiments were carried out on a glassy carbon rod held at -0.7 V \textit{vs.} NHE in TEOA/Na\(_2\)SO\(_4\) buffer (0.1 M each, pH 7).
Figure S5. Infra-red spectra of [CoCl(dimethylglyoximato)\textsubscript{2}(4-methoxypyridine)] (5 mM) in the presence of tetrabutylammonium bromide (0.3 M) in MeOH under an atmosphere of CO or N\textsubscript{2} at -0.8 V vs. Ag/Ag\textsuperscript{+}.

Figure S6. UV-visible spectroelectrochemical spectra of Ni\textsuperscript{I}P (0.25 mM) in the presence of tetrabutylammonium bromide (0.3 M) in MeOH under an atmosphere of CO at varying potentials.
Table S1. H$_2$ produced and Faradaic efficiency of NiP (0.5 mM in 0.1 M citrate buffer at pH 4.5) and CoP (0.5 mM in 0.1 M TEOA/Na$_2$SO$_4$ at pH 7) from CPE at –0.4 V (NiP for 60 min) and –0.7 V (CoP for 15 min) vs. NHE.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>NiP</th>
<th>CoP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$ / μmol</td>
<td>σ / μmol</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.05</td>
<td>0.29</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>CO</td>
<td>0.76</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table S2. H$_2$ produced by a Pt disk (1 mm) electrode (0.1 M citrate buffer at pH 4.5) from CPE at –0.4 V vs. NHE for 15 min.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$ / μmol</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.45</td>
</tr>
<tr>
<td>CO</td>
<td>0.03</td>
</tr>
<tr>
<td>N$_2$ after CO experiment</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Supporting References


End of ESI